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Effect of polyoxypropylene chain length on the critical micelle concentration of propylene oxide-ethylene oxide block copolymers*

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Abstract: In this work, the surface activity of block copolymer nonionic surfactants (RPE) has been determined, i.e., critical micelle concentration (CMC), surface excess concentration (Γ), surface area demand per molecule (A), surface tension at CMC (γ_{CMC}). A linear decrease of ln[CMC] vs number of oxypropylene units in copolymer molecule was observed. The change in the work of cohesion per oxypropylene group when passing from molecular into micellar state, calculated from the Shinoda equation, was 0.43kT for the studied compounds.

Key words: Nonionic surfactant, Propylene oxide-ethylene oxide block copolymers, Critical micelle concentration, Micellization
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INTRODUCTION

The hydrophobic properties of the polyoxypropylene chain have been utilized for many years in the preparation of surfactants. The polyoxypropylene grouping can contribute all the hydrophobicity of the surfactant or only the part of it, e.g., when forming the hydrophobic part of surfactant together with a hydrocarbon chain (Alexandridis and Yang, 2000; Gente *et al.*, 2004; Kelarakis *et al.*, 2001; Waton *et al.*, 2001). To the latter class of compounds belong the block copolymer surfactants obtained by the addition of propylene oxide to monofunctional initiators (e.g., aliphatic alcohols), followed by the addition of ethylene oxide. These compounds were named monofunctional all-block nonionics of the RPE type, where R is a monofunctional initiator; P and E are polyoxypropylene and polyoxyethylene chains. All the compounds described were polydisperse with respect to polyoxypropylene as well as to the polyoxypropylene chains. It was established that polyoxypropylene grouping caused the critical micelle concentration (CMC) of the RPE surfactants to decrease, and that the equivalent decrease of the CMC associated with one CH_2 aliphatic group was brought about by circa 2.5 oxypropylene units for n-hexyl, n-heptyl and 1,3-dialkoxy-2-propanols derivatives (Chlebicki and Majtyka, 1999; Kucharski and Chlebicki, 1974).

RPE block copolymer surfactants studied in this work have the following structure where R=$C_{12}H_{25}$, $C_{13}H_{27}$; m=0, 1, 2, 3 and 4; z=circa 8. Attempts were made to establish the exact relationship between the CMC and the number of propylene oxide (PO) units contained in the surfactant molecule.

$$RO(CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HO)_m(CH_2CH_2O)_zH$$

EXPERIMENTAL DETAILS

All block copolymer surfactants used in this work were obtained from Zhejiang Huangma Co., Ltd. All other auxiliary reagents were of analytical grade.

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The CMC values of the block copolymers were determined from the surface tension isotherms. The surface tension (γ) of aqueous solutions of the surfactants was measured using a JYW 2000A automatic tensiometer equipped with a du Nouy Pt-Ir ring. The measurements were performed at 20 °C.

RESULTS AND DISCUSSION

Surface activity depends on the length and the structure of the molecule or also on the kind of hydrophilic group. The surfactants studied in this work possessed a hydrophobic fragment consisting of a normal hydrocarbon chain and a polyoxypropylene chain. Surface tension (γ), as a function of the molar concentration natural logarithm (ln$C$), for aqueous solutions of the investigated block copolymers is depicted in Fig.1. They clearly illustrate the influence of polyoxypropylene chain length on surface activity. The calculated from surface tension isotherms values of CMC for RPE copolymers are presented in Table 1. These values are significantly lower than those in the case of the respective polyoxyethylenated alcohols. This comparison shows that the investigated copolymers with oxypropylene groups attached to hydrocarbon chains are relatively more hydrophobic. CMC values get smaller when the alkyl group changes from dodecyl to tridecyl (Table 1).

Table 1 Surface activity of block copolymer surfactants

Symbol	$10^5\times CMC$ (mol/dm^3)	γ_{CMC} (mN/m)	$10^6\times\Gamma$ (mol/m^2)	$10^{20}\times A$ (m^2)
$C_{12}E_8$	10.0	28.0	2.52	66
$C_{12}P_1E_8$	6.5	28.3	2.41	69
$C_{12}P_2E_8$	4.2	28.7	2.34	71
$C_{12}P_3E_8$	2.7	29.4	2.27	73
$C_{12}P_4E_8$	1.8	30.2	2.24	74
$C_{13}E_8$	3.2	27.1	2.44	68
$C_{13}P_2E_8$	1.3	27.8	2.27	73
$C_{13}P_3E_8$	0.9	28.1	2.21	75

As shown in Fig.2, the CMC values of copolymers decrease with increasing polyoxypropylene chain length and the relation between ln[CMC] and the number of PO units is linear. Such dependency makes it possible to establish the exact relationship between a polyoxypropylene chain and an aliphatic hydrocarbon CH_2 group with respect to their effect on the critical micelle concentration.

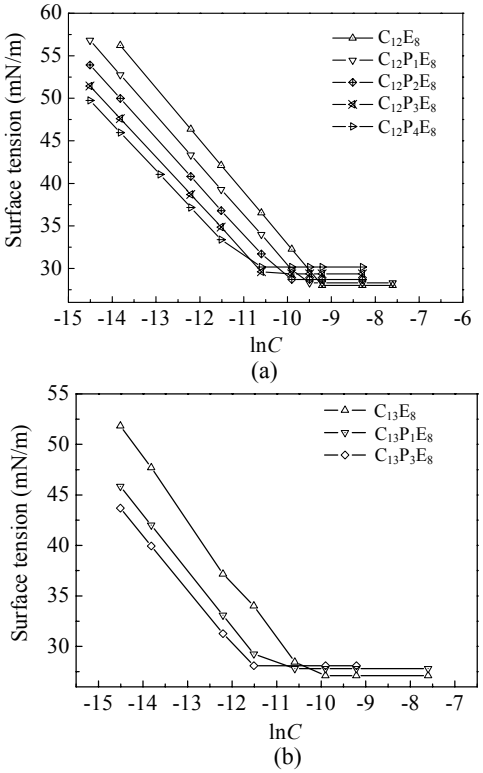

Fig.1 Surface tension isotherms. (a) Dodecyl derivatives; (b) Tridecyl derivatives

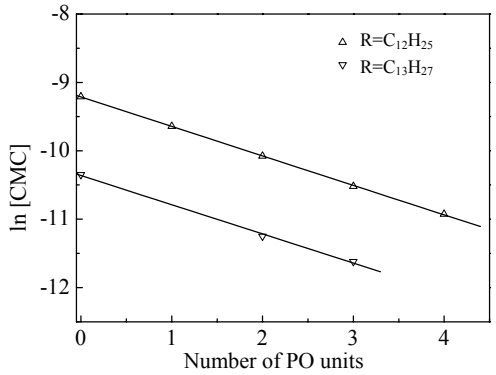

Fig.2 Relationship between ln[CMC] and the number of oxypropylene units in block copolymer

The relation between the CMC and the number of C atoms in the alkyl group of a normal nonionic surfactant can be expressed by the following equation (Shinoda *et al.*, 1963):

$$\ln[\mathrm{CMC}] = -\frac{n\cdot W_{\mathrm{CH_2}}}{\mathrm{k}T} + \text{const.} \qquad (1)$$

where CMC is the critical micelle concentration (mol/dm^3), n is the number of C atoms in hydrophobic group (e.g., alcohol), W_{CH_2} is the van der Waals energy of interaction per CH_2 group in adjacent hydrocarbon chains due to the micelle formation (the change of cohesion work), k is the Boltzmann constant, and T is the Kelvin temperature.

The above relation may be used to express the CMC of the RPE copolymers as a function of the polyxypropylene chain length as follows:

$$\ln[\mathrm{CMC}] = -\frac{n \cdot W_{CH_2}}{kT} - \frac{m \cdot W_{PO}}{kT} + \text{const.} \quad (2)$$

Where m is the number of PO units in the RPE copolymer; W_{PO} is the van der Waals energy of interaction per PO unit similar to W_{CH_2}. Since the relationships ln[CMC] vs n and ln[CMC] vs m are linear, it is possible to calculate W_{PO} for a given n and W_{CH_2} for a given m. From Fig.2, the values of W_{PO} are 0.43kT for dodecyl and tridecyl copolymer series, respectively. The values of W_{CH_2} are 1.14kT–1.17kT and are in good agreement with those of polyoxyethylene alcohols. If the work of cohesion is a measure of micelle formation ability, then the equivalent of CH_2 in an aliphatic alcohol group is 2.65–2.72 oxypropylene units.

The surface tension data allowed us to calculate the surface excess concentration (Γ) at the aqueous solution–air interface based on the Gibbs adsorption equation

$$\mathrm{d}\gamma/\mathrm{dln}a = -\mathrm{R}T\Gamma \quad (3)$$

where a is the activity(at low surfactant concentration may be replaced by concentration). Surface excess may be determined from the slope of a surface tension isotherm. Hence, the area, A, occupied by one compound molecule in the surface layer (assuming the layer to be monomolecular), can be found from the equation:

$$A = 1/\mathrm{N}\Gamma \quad (4)$$

where N is Avogadro constant. The values of Γ and A obtained in this way are presented in Table 1. From the presented Γ values it can be seen that RPE-type copolymers are adsorbed on the aqueous solution/air interfacial surface to a lesser extent than the respective polyoxyethylenated alcohols. Therefore, the surface occupied by molecules of block copolymer in a monomolecular adsorption layer is much bigger. For example for $C_{12}P_3E_8$ and $C_{13}P_3E_8$, Γ is 2.27 and 2.21 μmol/m^2, A is 73 and 75 Å^2, whereas for $C_{12}E_8$ and $C_{13}E_8$ the values of Γ are 2.52 and 2.44 μmol/m^2, and A is 66 and 68 Å^2. This means that molecules of the investigated block copolymers assume a coil shape at the interfacial surface, which makes them different from polyoxyethylenated alcohols in which the hydrophobic fragment is almost straight.

Both of these studies will be further investigated by studying a variety of other systems.

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